

4 - EFDC WATER QUALITY MODEL

4.1 Introduction

The central issues in the water quality model are primary production of carbon by algae and concentration of dissolved oxygen. Primary production provides the energy required by the ecosystem to function. However, excessive primary production is detrimental since its decomposition in the water and sediments consumes oxygen. Dissolved oxygen is necessary to support the life functions of higher organisms and is considered an indicator of the health of estuarine systems. To predict primary production and dissolved oxygen, a large suite of model state variables is necessary (Table 4-1). The nitrate state variable in the model represents the sum of nitrate and nitrite nitrogen. The three variables (salinity, water temperature, and total suspended solids) needed for computation of the above 21 state variables are provided by the EFDC hydrodynamic model. The interactions among the state variables is illustrated in Figure 4-1. The kinetic processes included in the EFDC water quality model are mostly from the Chesapeake Bay three-dimensional water quality model, CE-QUAL-ICM (Cерco and Cole 1994). The kinetic sources and sinks, as well as the external loads for each state variable, are described in Sections 4.3 to 4.11. The kinetic processes include the exchange of fluxes at the sediment-water interface, including sediment oxygen demand, which are explained in Section 5 (EFDC Sediment Process Model) of this report. The description of the EFDC water column water quality model in this section is from Park et al. (1995).

Table 4-1. EFDC model water quality state variables

(1) cyanobacteria	(12) labile particulate organic nitrogen
(2) diatom algae	(13) dissolved organic nitrogen
(3) green algae	(14) ammonia nitrogen
(4) refractory particulate organic carbon	(15) nitrate nitrogen
(5) labile particulate organic carbon	(16) particulate biogenic silica
(6) dissolved organic carbon	(17) dissolved available silica
(7) refractory particulate organic phosphorus	(18) chemical oxygen demand
(8) labile particulate organic phosphorus	(19) dissolved oxygen
(9) dissolved organic phosphorus	(20) total active metal
(10) total phosphate	(21) fecal coliform bacteria
(11) refractory particulate organic nitrogen	(22) macroalgae

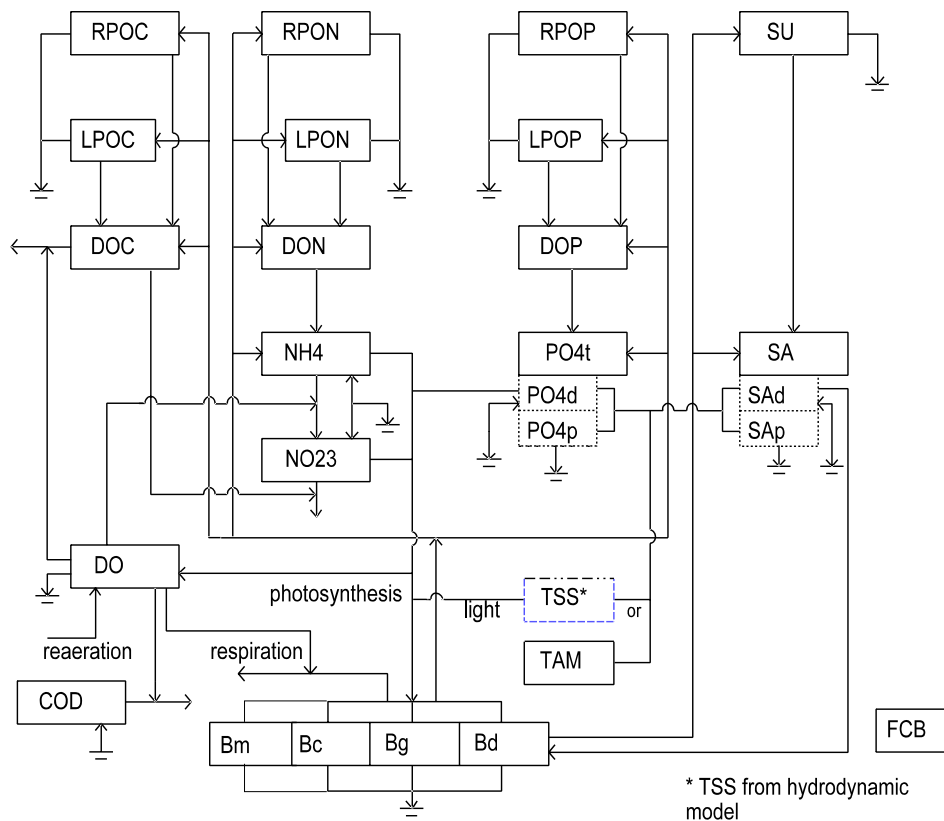


Figure 4-1. Schematic diagram for the EFDC water column water quality model

4.1.1 Algae

Algae are grouped into four model classes: cyanobacteria, diatoms, greens, and macroalgae. The grouping is based upon the distinctive characteristics of each class and upon the significant role the characteristics play in the ecosystem. Cyanobacteria, commonly called blue-green algae, are characterized by their abundance (as picoplankton) in saline water and by their bloom-forming characteristics in fresh water. Cyanobacteria are unique in that some species fix atmospheric nitrogen, although nitrogen fixers are not believed to be predominant in many river systems. Diatoms are distinguished by their requirement of silica as a nutrient to form cell walls. Diatoms are large algae characterized by high settling velocities. Settling of spring diatom blooms to the sediments may be a significant source of carbon for sediment oxygen demand. Algae that do not fall into the preceding two groups are lumped into the heading of green algae. Green algae settle at a rate intermediate between cyanobacteria and diatoms and are subject to greater grazing pressure than cyanobacteria. Macroalgae are

almost always attached to a stable substrate and are therefore most abundant in the areas of harbors and near shore. The waters in many stream systems are characterized by various rooted macrophytes and periphyton. All species of macroalgae in this study have been lumped into a single class of macroalgae. Because of their attachment to the substrate, they are limited to growing in the bottom water-column layer and are not subject to physical transport.

4.1.2 Organic Carbon

Three organic carbon state variables are considered: dissolved, labile particulate, and refractory particulate. Labile and refractory distinctions are based upon the time scale of decomposition. Labile organic carbon decomposes on a time scale of days to weeks whereas refractory organic carbon requires more time. Labile organic carbon decomposes rapidly in the water column or the sediments. Refractory organic carbon decomposes slowly, primarily in the sediments, and may contribute to sediment oxygen demand years after deposition.

4.1.3 Nitrogen

Nitrogen is first divided into organic and mineral fractions. Organic nitrogen state variables are dissolved organic nitrogen, labile particulate organic nitrogen, and refractory particulate organic nitrogen. Two mineral nitrogen forms are considered: ammonium and nitrate. Both are utilized to satisfy algal nutrient requirements, although ammonium is preferred from thermodynamic considerations. The primary reason for distinguishing the two is that ammonium is oxidized by nitrifying bacteria into nitrate. This oxidation can be a significant sink of oxygen in the water column and sediments. An intermediate in the complete oxidation of ammonium, nitrite, also exists. Nitrite concentrations are usually much less than nitrate, and for modeling purposes, nitrite is combined with nitrate. Hence the nitrate state variable actually represents the sum of nitrate plus nitrite.

4.1.4 Phosphorus

As with carbon and nitrogen, organic phosphorus is considered in three states: dissolved, labile particulate, and refractory particulate. Only a single mineral form, total phosphate, is considered. Total phosphate exists as several states within the model ecosystem: dissolved phosphate, phosphate sorbed to inorganic solids, and phosphate incorporated in algal cells. Equilibrium partition coefficients are used to distribute the total among the three states.

4.1.5 Silica

Silica is divided into two state variables: available silica and particulate biogenic silica. Available silica is primarily dissolved and can be utilized by diatoms. Particulate biogenic silica cannot be utilized. In the model, particulate biogenic silica is produced through diatom mortality. Particulate biogenic silica undergoes dissolution to available silica or else settles to the bottom sediments.

4.1.6 Chemical Oxygen Demand

In the context of this study, chemical oxygen demand is the concentration of reduced substances that are oxidizable by inorganic means. The primary component of chemical oxygen demand is sulfide released from sediments. Oxidation of sulfide to sulfate may remove substantial quantities of dissolved oxygen from the water column.

4.1.7 Dissolved Oxygen

Dissolved oxygen is required for the existence of higher life forms. Oxygen availability determines the distribution of organisms and the flows of energy and nutrients in an ecosystem. Dissolved oxygen is a central component of the water quality model.

4.1.8 Total Active Metal

Both phosphate and dissolved silica sorb to inorganic solids, primarily iron and manganese. Sorption and subsequent settling is one pathway for removal of phosphate and silica from the water column.

Consequently, the concentration and transport of iron and manganese are represented in the model.

Limited data do not allow a complete treatment of iron and manganese chemistry, however. Rather, a single-state variable, total active metal, is defined as the total concentration of metals that are active in phosphate and silica transport. Total active metal is partitioned between particulate and dissolved phases by an oxygen-dependent partition coefficient.

4.1.9 Salinity

Salinity is a conservative tracer that provides verification of the transport component of the model and facilitates examination of conservation of mass. Salinity also influences the dissolved oxygen saturation concentration and is used in the determination of kinetics constants that differ in saline and fresh water.

4.1.10 Temperature

Temperature is a primary determinant of the rate of biochemical reactions. Reaction rates increase as a function of temperature, although extreme temperatures result in the mortality of organisms.

4.2 Conservation of Mass Equation

The governing mass-balance equation for each of the water quality state variables may be expressed as:

$$\frac{\partial C}{\partial t} + \frac{\partial(uC)}{\partial x} + \frac{\partial(vC)}{\partial y} + \frac{\partial(wC)}{\partial z} =$$

$$\frac{\partial}{\partial x} \left(K_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial C}{\partial z} \right) + S_C \quad (4-1)$$

- C = concentration of a water quality state variable
 u, v, w = velocity components in the x-, y-, and z-directions, respectively
 K_x, K_y, K_z = turbulent diffusivities in the x-, y-, and z-directions, respectively
 S_C = internal and external sources and sinks per unit volume.

The last three terms on the left-hand side (LHS) of Eq. 4-1 account for the advective transport, and the first three terms on the right-hand side (RHS) of Eq. 4-1 account for the diffusive transport. These six terms for physical transport are analogous to, and thus the numerical method of solution is the same as, those in the mass-balance equation for salinity in the hydrodynamic model (Hamrick 1992a). The last term in Eq. 4-1 represents the kinetic processes and external loads for each of the state variables. The present model solves Eq. 4-1 after decoupling the kinetic terms from the physical transport terms. The solution scheme for both the physical transport (Hamrick 1992a) and the kinetic equations is second-order accurate.

The governing mass-balance equation for water quality state variables (Eq. 4-1) consists of physical transport, advective and diffusive, and kinetic processes. When solving Eq. 4-1, the kinetic terms are decoupled from the physical transport terms. The mass-balance equation for physical transport only, which takes the same form as the salt-balance equation, is:

$$\frac{\partial C}{\partial t} + \frac{\partial(uC)}{\partial x} + \frac{\partial(vC)}{\partial y} + \frac{\partial(wC)}{\partial z} = \frac{\partial}{\partial x} \left(K_x \frac{\partial C}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_y \frac{\partial C}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_z \frac{\partial C}{\partial z} \right) \quad (4-2)$$

The equation for kinetic processes only, which will be referred to as the kinetic equation, is:

$$\frac{\partial C}{\partial t} = S_C \quad (4-3)$$

which may be expressed as:

$$\frac{\partial C}{\partial t} = K \cdot C + R \quad (4-4)$$

where K is kinetic rate (time⁻¹) and R is source/sink term (mass volume⁻¹ time⁻¹). Equation 4-4 is obtained by linearizing some terms in the kinetic equations, mostly Monod type expressions. Hence, K and R are known values in Eq. 4-4. Equation 4-2 is identical to, and thus its numerical method of solution is the same as, the mass-balance equation for salinity (Hamrick 1992a).

The remainder of this chapter details the kinetics portion of the mass-conservation equation for each state variable. Parameters are defined where they first appear. All parameters are listed, in alphabetical order, in an appendix. For consistency with reported rate coefficients, kinetics are detailed using a temporal dimension of days. Within the CE-QUAL-ICM computer code, kinetics sources and sinks are converted to a dimension of seconds before employment in the mass-conservation equation.

4.3 Algae

Algae, which occupies a central role in the model (Figure 4-1), are grouped into three model state variables: cyanobacteria (blue-green algae), diatoms, and green algae. The subscript, **x**, is used to denote four algal groups: **c** for cyanobacteria, **d** for diatoms, **g** for green algae, and **m** for macroalgae. Sources and sinks included in the model are

- growth (production)
- basal metabolism
- predation
- settling
- external loads

Equations describing these processes are largely the same for the four algal groups with differences in the values of parameters in the equations. The kinetic equation describing these processes is:

$$\frac{\partial B_x}{\partial t} = (P_x - BM_x - PR_x)B_x + \frac{\partial}{\partial z}(WS_x \cdot B_x) + \frac{WB_x}{V} \quad (4-5)$$

B_x = algal biomass of algal group x (g C m⁻³)

t = time (day)

P_x = production rate of algal group x (day⁻¹)

BM_x = basal metabolism rate of algal group x (day⁻¹)

PR_x = predation rate of algal group x (day⁻¹)

WS_x = settling velocity of algal group x (m day⁻¹)

WB_x = external loads of algal group x (g C day⁻¹)

V = cell volume (m³).

The model simulates the total biomass of the macroalgae rather than the size of the macroalgae; therefore, they can be treated as other groups of algae. Since macroalgae attach to the bottom, they are limited to growing in the bottom layer only and are not be transported through water movement.

4.3.1 Production (Algal Growth)

Algal growth depends on nutrient availability, ambient light, and temperature. The effects of these processes are considered to be multiplicative:

$$P_x = PM_x \cdot f_1(N) \cdot f_2(I) \cdot f_3(T) \quad (4-6)$$

PM_x = maximum growth rate under optimal conditions for algal group x (day^{-1})

$f_1(N)$ = effect of suboptimal nutrient concentration ($0 \leq f_1 \leq 1$)

$f_2(I)$ = effect of suboptimal light intensity ($0 \leq f_2 \leq 1$)

$f_3(T)$ = effect of suboptimal temperature ($0 \leq f_3 \leq 1$).

The freshwater cyanobacteria may undergo rapid mortality in salt water, e.g., freshwater organisms in the Potomac River (Thomann et al. 1985). For the freshwater organisms, the increased mortality may be included in the model by retaining the salinity toxicity term in the growth equation for cyanobacteria:

$$P_c = PM_c \cdot f_1(N) \cdot f_2(I) \cdot f_3(T) \cdot f_4(S) \quad (4-7)$$

$f_4(S)$ = effect of salinity on cyanobacteria growth ($0 \leq f_4 \leq 1$).

Activation of the salinity toxicity term, $f_4(S)$, is an option in the source code.

4.3.2 Effect of Nutrients on Algal Growth

Using Liebig's "law of the minimum" (Odum 1971) that growth is determined by the nutrient in least supply, the nutrient limitation for growth of cyanobacteria and green algae is expressed as:

$$f_1(N) = \text{minimum} \left(\frac{NH4 + NO3}{KHN_x + NH4 + NO3}, \frac{PO4d}{KHP_x + PO4d} \right) \quad (4-8)$$

$NH4$ = ammonium nitrogen concentration (g N m^{-3})

$NO3$ = nitrate nitrogen concentration (g N m^{-3})

KHN_x = half-saturation constant for nitrogen uptake for algal group x (g N m^{-3})

$PO4d$ = dissolved phosphate phosphorus concentration (g P m^{-3})

KHP_x = half-saturation constant for phosphorus uptake for algal group x (g P m^{-3}).

Some cyanobacteria, e.g., *Anabaena*, can fix nitrogen from atmosphere and thus are not limited by nitrogen. Hence, Eq. 4-8 is not applicable to the growth of nitrogen fixers.

Since diatoms require silica as well as nitrogen and phosphorus for growth, the nutrient limitation for diatoms is expressed as:

$$f_1(N) = \text{minimum} \left(\frac{NH4 + NO3}{KHN_d + NH4 + NO3}, \frac{PO4d}{KHP_d + PO4d}, \frac{SAd}{KHS + SAd} \right) \quad (4-9)$$

SAd = concentration of dissolved available silica (g Si m⁻³)

KHS = half-saturation constant for silica uptake for diatoms (g Si m⁻³).

4.3.3 Effect of Light on Algal Growth

The daily and vertically integrated form of Steele's equation is:

$$f_2(I) = \frac{2.718 \cdot FD}{K_{ess} \cdot \Delta z} (e^{-\alpha_B} - e^{-\alpha_T}) \quad (4-10)$$

$$\alpha_B = \frac{I_o}{FD \cdot (I_s)_x} \cdot \exp(-K_{ess} [H_T + \Delta z]) \quad (4-11)$$

$$\alpha_T = \frac{I_o}{FD \cdot (I_s)_x} \cdot \exp(-K_{ess} \cdot H_T) \quad (4-12)$$

FD = fractional daylength (0 ≤ FD ≤ 1)

K_{ess} = total light extinction coefficient (m⁻¹)

Δz = layer thickness (m)

I_o = daily total light intensity at water surface (langley's day⁻¹)

(I_s)_x = optimal light intensity for algal group x (langley's day⁻¹)

H_T = depth from the free surface to the top of the layer (m).

Light extinction in the water column consists of three fractions in the model: a background value dependent on water color, extinction due to suspended particles, and extinction due to light absorption by ambient chlorophyll:

$$K_{ess} = K_{e_b} + K_{e_{TSS}} \cdot TSS + K_{e_{chl}} \cdot \sum_{x=c,d,g} \left(\frac{B_x}{CChl_x} \right) \quad (4-13)$$

K_{e_b} = background light extinction (m⁻¹)

K_{e_{TSS}} = light extinction coefficient for total suspended solid (m⁻¹ per g m⁻³)

TSS = total suspended solid concentration (g m⁻³) provided from the hydrodynamic model

K_{e_{chl}} = light extinction coefficient for chlorophyll 'a' (m⁻¹ per mg Chl m⁻³)

CChl_x = carbon-to-chlorophyll ratio in algal group x (g C per mg Chl).

Since macroalgae only attach to the bottom, they are not included in computation of the light extinction. Self shading is not considered for macroalgae for the present model. For a model application that does not simulate TSS, the K_{e_{TSS}} term may be set to zero and K_{e_b} may be estimated to include light extinction due to suspended solid.

Optimal light intensity (I_s) for photosynthesis depends on algal taxonomy, duration of exposure, temperature, nutritional status, and previous acclimation. Variations in I_s are largely due to adaptations by algae intended to maximize production in a variable environment. Steel (1962) noted the result of adaptations is that optimal intensity is a consistent fraction (approximately 50%) of daily intensity. Kremer and Nixon (1981) reported an analogous finding that maximum algal growth occurs at a constant depth (approximately 1 m) in the water column. Their approach is adopted so that optimal intensity is expressed as:

$$(I_s)_x = \text{maximum} \{ (I_o)_{avg} \cdot e^{-K_{ess}(D_{opt})_x}, (I_s)_{min} \} \quad (4-14)$$

$(D_{opt})_x$ = depth of maximum algal growth for algal group x (m)

$(I_o)_{avg}$ = adjusted surface light intensity (langleys day⁻¹).

A minimum, $(I_s)_{min}$, in Eq. 4-14 is specified so that algae do not thrive at extremely low light levels. The time required for algae to adapt to changes in light intensity is recognized by estimating $(I_s)_x$ based on a time-weighted average of daily light intensity:

$$(I_o)_{avg} = CI_a \cdot I_o + CI_b \cdot I_1 + CI_c \cdot I_2 \quad (4-15)$$

I_1 = daily light intensity 1 day preceding model day (langleys day⁻¹)

I_2 = daily light intensity 2 days preceding model day (langleys day⁻¹)

CI_a, CI_b, CI_c = weighting factors for I_o, I_1 and I_2 , respectively: $CI_a + CI_b + CI_c = 1$.

4.3.4 Effect of Temperature on Algal Growth

A Gaussian probability curve is used to represent temperature dependency of algal growth:

$$\begin{aligned} f_3(T) &= \exp(-KTG1_x[T - TM_x]^2) & \text{if } T \leq TM_x \\ &= \exp(-KTG2_x[TM_x - T]^2) & \text{if } T > TM_x \end{aligned} \quad (4-16)$$

T = temperature (°C) provided from the hydrodynamic model

TM_x = optimal temperature for algal growth for algal group x (°C)

$KTG1_x$ = effect of temperature below TM_x on growth for algal group x (°C⁻²)

$KTG2_x$ = effect of temperature above TM_x on growth for algal group x (°C⁻²).

4.3.5 Effect of Salinity on Growth of Freshwater Cyanobacteria

The growth of freshwater cyanobacteria in salt water is limited by:

$$f_4(S) = \frac{STOX^2}{STOX^2 + S^2} \quad (4-17)$$

$STOX$ = salinity at which Microcystis growth is halved (ppt)

S = salinity in water column (ppt) provided from the hydrodynamic model.

4.3.6 Algal Basal Metabolism

Algal biomass in the present model decreases through basal metabolism (respiration and excretion) and predation. Basal metabolism in the present model is the sum of all internal processes that decrease algal biomass and consists of two parts; respiration and excretion. In basal metabolism, algal matter (carbon, nitrogen, phosphorus, and silica) is returned to organic and inorganic pools in the environment, mainly to dissolved organic and inorganic matter. Respiration, which may be viewed as a reversal of production, consumes dissolved oxygen. Basal metabolism is considered to be an exponentially increasing function of temperature:

$$BM_x = BMR_x \cdot \exp(KTB_x[T - TR_x]) \quad (4-18)$$

BMR_x = basal metabolism rate at TR_x for algal group x (day^{-1})

KTB_x = effect of temperature on metabolism for algal group x ($^{\circ}\text{C}^{-1}$)

TR_x = reference temperature for basal metabolism for algal group x ($^{\circ}\text{C}$).

4.3.7 Algal Predation

The present model does not include zooplankton. Instead, a constant rate is specified for algal predation, which implicitly assumes zooplankton biomass is a constant fraction of algal biomass. An equation similar to that for basal metabolism (Eq. 4-18) is used for predation:

$$PR_x = PRR_x \cdot \exp(KTB_x[T - TR_x]) \quad (4-19)$$

PRR_x = predation rate at TR_x for algal group x (day^{-1}).

The difference between predation and basal metabolism lies in the distribution of the end products of the two processes. In predation, algal matter (carbon, nitrogen, phosphorus, and silica) is returned to organic and inorganic pools in the environment, mainly to particulate organic matter. The predation for macroalgae is a lumped parameter that includes losses due to grazing, frond breakage, and other losses. This implicitly assumes that the losses are a fraction of the biomass.

4.3.8 Algal Settling

Settling velocities for four algal groups, WS_c , WS_d , WS_g , and WS_m , are specified as an input. Seasonal variations in settling velocity of diatoms can be accounted for by specifying time-varying WS_d .

4.4 Organic Carbon

The present model has three state variables for organic carbon: refractory particulate, labile particulate, and dissolved.

4.4.1 Particulate Organic Carbon

Labile and refractory distinctions are based on the time scale of decomposition. Labile particulate organic carbon with a decomposition time scale of days to weeks decomposes rapidly in the water column or in the sediments. Refractory particulate organic carbon with a longer-than-weeks decomposition time scale decomposes slowly, primarily in the sediments, and may contribute to sediment oxygen demand years after decomposition. For labile and refractory particulate organic carbon, sources and sinks included in the model are (Fig. 4-1):

- algal predation
- dissolution to dissolved organic carbon
- settling
- external loads.

The governing equations for refractory and labile particulate organic carbons are:

$$\frac{\partial RPOC}{\partial t} = \sum_{x=c,d,g,m} FCRP \cdot PR_x \cdot B_x - K_{RPOC} \cdot RPOC + \frac{\partial}{\partial z} (WS_{RP} \cdot RPOC) + \frac{WRPOC}{V} \quad (4-20)$$

$$\frac{\partial LPOC}{\partial t} = \sum_{x=c,d,g,m} FCLP \cdot PR_x \cdot B_x - K_{LPOC} \cdot LPOC + \frac{\partial}{\partial z} (WS_{LP} \cdot LPOC) + \frac{WLPOC}{V} \quad (4-21)$$

RPOC = concentration of refractory particulate organic carbon (g C m⁻³)

LPOC = concentration of labile particulate organic carbon (g C m⁻³)

FCRP = fraction of predated carbon produced as refractory particulate organic carbon

FCLP = fraction of predated carbon produced as labile particulate organic carbon

K_{RPOC} = dissolution rate of refractory particulate organic carbon (day⁻¹)

K_{LPOC} = dissolution rate of labile particulate organic carbon (day⁻¹)

WS_{RP} = settling velocity of refractory particulate organic matter (m day⁻¹)

WS_{LP} = settling velocity of labile particulate organic matter (m day⁻¹)

WRPOC = external loads of refractory particulate organic carbon (g C day⁻¹)

WLPOC = external loads of labile particulate organic carbon (g C day⁻¹).

4.4.2 Dissolved Organic Carbon

Sources and sinks for dissolved organic carbon included in the model are (Fig. 4-1):

- algal excretion (exudation) and predation
- dissolution from refractory and labile particulate organic carbon
- heterotrophic respiration of dissolved organic carbon (decomposition)
- denitrification

- external loads

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial DOC}{\partial t} = & \sum_{x=c,d,g,m} \left(\left[FCD_x + (1 - FCD_x) \frac{KHR_x}{KHR_x + DO} \right] BM_x + FCDP \cdot PR_x \right) \cdot B_x \\ & + K_{RPOC} \cdot RPOC + K_{LPOC} \cdot LPOC - K_{HR} \cdot DOC - Denit \cdot DOC + \frac{WDOC}{V} \quad (4-22) \end{aligned}$$

DOC = concentration of dissolved organic carbon (g C m⁻³)

FCD_x = fraction of basal metabolism exuded as dissolved organic carbon at infinite dissolved oxygen concentration for algal group x

KHR_x = half-saturation constant of dissolved oxygen for algal dissolved organic carbon excretion for group x (g O₂ m⁻³)

DO = dissolved oxygen concentration (g O₂ m⁻³)

FCDP = fraction of predated carbon produced as dissolved organic carbon

K_{HR} = heterotrophic respiration rate of dissolved organic carbon (day⁻¹)

Denit = denitrification rate (day⁻¹) given in Eq. 4-34

WDOC = external loads of dissolved organic carbon (g C day⁻¹).

The remainder of this section explains each term in Equations 4-20 to 4-22.

4.4.3 Effect of Algae on Organic Carbon

The terms within summation (\sum) in Equations 4-20 to 4-22 account for the effects of algae on organic carbon through basal metabolism and predation.

4.4.3.1 Basal metabolism. Basal metabolism, consisting of respiration and excretion, returns algal matter (carbon, nitrogen, phosphorus, and silica) back to the environment. Loss of algal biomass through basal metabolism is (Eq. 4-18):

$$\frac{\partial B_x}{\partial t} = - BM_x \cdot B_x \quad (4-23)$$

which indicates that the total loss of algal biomass due to basal metabolism is independent of ambient dissolved oxygen concentration. In this model, it is assumed that the distribution of total loss between respiration and excretion is constant as long as there is sufficient dissolved oxygen for algae to respire. Under that condition, the losses by respiration and excretion may be written as:

$$(1 - FCD_x) \cdot BM_x \cdot B_x \quad \text{due to respiration} \quad (4-24)$$

$$FCD_x \cdot BM_x \cdot B_x \quad \text{due to excretion} \quad (4-25)$$

where FCD_x is a constant of value between 0 and 1. Algae cannot respire in the absence of oxygen, however. Although the total loss of algal biomass due to basal metabolism is oxygen-independent (Eq. 4-23), the distribution of total loss between respiration and excretion is oxygen-dependent. When oxygen level is high, respiration is a large fraction of the total. As dissolved oxygen becomes scarce, excretion becomes dominant. Thus, Eq. 4-24 represents the loss by respiration only at high oxygen levels. In general, Eq. 4-24 can be decomposed into two fractions as a function of dissolved oxygen availability:

$$(1 - FCD_x) \frac{DO}{KHR_x + DO} BM_x \cdot B_x \quad \text{due to respiration} \quad (4-26)$$

$$(1 - FCD_x) \frac{KHR_x}{KHR_x + DO} BM_x \cdot B_x \quad \text{due to excretion} \quad (4-27)$$

Equation 4-26 represents the loss of algal biomass by respiration, and Eq. 4-27 represents additional excretion due to insufficient dissolved oxygen concentration. The parameter KHR_x , which is defined as the half-saturation constant of dissolved oxygen for algal dissolved organic carbon excretion in Eq. 4-22, can also be defined as the half-saturation constant of dissolved oxygen for algal respiration in Eq. 4-26.

Combining Equations 4-25 and 4-27, the total loss due to excretion is:

$$\left(FCD_x + (1 - FCD_x) \frac{KHR_x}{KHR_x + DO} \right) BM_x \cdot B_x \quad (4-28)$$

Equations 4-26 and 4-28 combine to give the total loss of algal biomass due to basal metabolism, $BM_x \cdot B_x$ (Eq. 4-23). The definition of FCD_x in Eq. 4-22 becomes apparent in Eq. 4-28; i.e., fraction of basal metabolism exuded as dissolved organic carbon at infinite dissolved oxygen concentration. At zero oxygen level, 100% of total loss due to basal metabolism is by excretion regardless of FCD_x . The end carbon product of respiration is primarily carbon dioxide, an inorganic form not considered in the present model, while the end carbon product of excretion is primarily dissolved organic carbon. Therefore, Eq. 4-28, that appears in Eq. 4-22, represents the contribution of excretion to dissolved organic carbon, and there is no source term for particulate organic carbon from algal basal metabolism in Equations 4-20 and 4-21.

4.4.3.2 Predation. Algae produce organic carbon through the effects of predation. Zooplankton take up and redistribute algal carbon through grazing, assimilation, respiration, and excretion. Since zooplankton are not included in the model, routing of algal carbon through zooplankton predation is simulated by

empirical distribution coefficients in Equations 4-20 to 4-22; FCRP, FCLP, and FCDP. The sum of these three predation fractions should be unity.

4.4.4 Heterotrophic Respiration and Dissolution

The second term on the RHS of Equations 4-20 and 4-21 represents dissolution of particulate to dissolved organic carbon and the third term in the second line of Eq. 4-22 represents heterotrophic respiration of dissolved organic carbon. The oxic heterotrophic respiration is a function of dissolved oxygen: the lower the dissolved oxygen, the smaller the respiration term becomes. Heterotrophic respiration rate, therefore, is expressed using a Monod function of dissolved oxygen:

$$K_{HR} = \frac{DO}{KHOR_{DO} + DO} K_{DOC} \quad (4-29)$$

$KHOR_{DO}$ = oxic respiration half-saturation constant for dissolved oxygen ($\text{g O}_2 \text{ m}^{-3}$)

K_{DOC} = heterotrophic respiration rate of dissolved organic carbon at infinite dissolved oxygen concentration (day^{-1}).

Dissolution and heterotrophic respiration rates depend on the availability of carbonaceous substrate and on heterotrophic activity. Algae produce labile carbon that fuels heterotrophic activity: dissolution and heterotrophic respiration do not require the presence of algae though, and may be fueled entirely by external carbon inputs. In the model, algal biomass, as a surrogate for heterotrophic activity, is incorporated into formulations of dissolution and heterotrophic respiration rates. Formulations of these rates require specification of algal-dependent and algal-independent rates:

$$K_{RPOC} = (K_{RC} + K_{RCalg} \sum_{x=c,d,g} B_x) \cdot \exp(KT_{HDR}[T - TR_{HDR}]) \quad (4-30)$$

$$K_{LPOC} = (K_{LC} + K_{LCalg} \sum_{x=c,d,g} B_x) \cdot \exp(KT_{HDR}[T - TR_{HDR}]) \quad (4-31)$$

$$K_{DOC} = (K_{DC} + K_{DCalg} \sum_{x=c,d,g} B_x) \cdot \exp(KT_{MNL}[T - TR_{MNL}]) \quad (4-32)$$

K_{RC} = minimum dissolution rate of refractory particulate organic carbon (day^{-1})

K_{LC} = minimum dissolution rate of labile particulate organic carbon (day^{-1})

K_{DC} = minimum respiration rate of dissolved organic carbon (day^{-1})

K_{RCalg} , K_{LCalg} = constants that relate dissolution of refractory and labile particulate organic carbon, respectively, to algal biomass (day^{-1} per g C m^{-3})

K_{DCalg} = constant that relates respiration to algal biomass (day^{-1} per g C m^{-3})

KT_{HDR} = effect of temperature on hydrolysis of particulate organic matter ($^{\circ}\text{C}^{-1}$)

TR_{HDR} = reference temperature for hydrolysis of particulate organic matter ($^{\circ}\text{C}$)

KT_{MNL} = effect of temperature on mineralization of dissolved organic matter ($^{\circ}C^{-1}$)

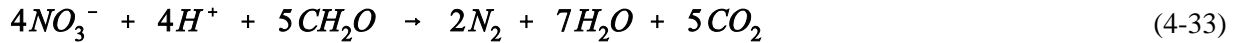
TR_{MNL} = reference temperature for mineralization of dissolved organic matter ($^{\circ}C$).

Equations 4-30 to 4-32 have exponential functions that relate rates to temperature.

In the present model, the term "hydrolysis" is defined as the process by which particulate organic matter is converted to dissolved organic form, and thus includes both dissolution of particulate carbon and hydrolysis of particulate phosphorus and nitrogen. Therefore, the parameters, KT_{HDR} and TR_{HDR} , are also used for the temperature effects on hydrolysis of particulate phosphorus (Equations 4-28 and 4-29) and nitrogen (Equations 4-54 and 4-55). The term "mineralization" is defined as the process by which dissolved organic matter is converted to dissolved inorganic form, and thus includes both heterotrophic respiration of dissolved organic carbon and mineralization of dissolved organic phosphorus and nitrogen. Therefore, the parameters, KT_{MNL} and TR_{MNL} , are also used for the temperature effects on mineralization of dissolved phosphorus (Eq. 4-46) and nitrogen (Eq. 4-56).

4.4.5 Effect of Denitrification on Dissolved Organic Carbon

As oxygen is depleted from natural systems, organic matter is oxidized by the reduction of alternate electron acceptors. Thermodynamically, the first alternate acceptor reduced in the absence of oxygen is nitrate. The reduction of nitrate by a large number of heterotrophic anaerobes is referred to as denitrification, and the stoichiometry of this reaction is (Stumm and Morgan 1981):



The last term in Eq. 4-22 accounts for the effect of denitrification on dissolved organic carbon. The kinetics of denitrification in the model are first-order:

$$Denit = \frac{KHOR_{DO}}{KHOR_{DO} + DO} \frac{NO_3}{KHDN_N + NO_3} AANOX \cdot K_{DOC} \quad (4-34)$$

$KHDN_N$ = denitrification half-saturation constant for nitrate ($g\ N\ m^{-3}$)

$AANOX$ = ratio of denitrification rate to oxic dissolved organic carbon respiration rate.

In Eq. 4-34, the dissolved organic carbon respiration rate, K_{DOC} , is modified so that significant decomposition via denitrification occurs only when nitrate is freely available and dissolved oxygen is depleted. The ratio, $AANOX$, makes the anoxic respiration slower than oxic respiration. Note that K_{DOC} , defined in Eq. 4-32, includes the temperature effect on denitrification.

4.5 Phosphorus

The present model has four state variables for phosphorus: three organic forms (refractory particulate, labile particulate, and dissolved) and one inorganic form (total phosphate).

4.5.1 Particulate Organic Phosphorus

For refractory and labile particulate organic phosphorus, sources and sinks included in the model are (Fig. 4-1):

- algal basal metabolism and predation
- dissolution to dissolved organic phosphorus
- settling
- external loads.

The kinetic equations for refractory and labile particulate organic phosphorus are:

$$\begin{aligned} \frac{\partial RPOP}{\partial t} = & \sum_{x=c,d,g,m} (FPR_x \cdot BM_x + FPRP \cdot PR_x) APC \cdot B_x - K_{RPOP} \cdot RPOP \\ & + \frac{\partial}{\partial z} (WS_{RP} \cdot RPOP) + \frac{WRPOP}{V} \end{aligned} \quad (4-35)$$

$$\begin{aligned} \frac{\partial LPOP}{\partial t} = & \sum_{x=c,d,g,m} (FPL_x \cdot BM_x + FPLP \cdot PR_x) APC \cdot B_x - K_{LPOP} \cdot LPOP \\ & + \frac{\partial}{\partial z} (WS_{LP} \cdot LPOP) + \frac{WLPOP}{V} \end{aligned} \quad (4-36)$$

RPOP = concentration of refractory particulate organic phosphorus (g P m⁻³)

LPOP = concentration of labile particulate organic phosphorus (g P m⁻³)

FPR_x = fraction of metabolized phosphorus by algal group x produced as refractory particulate organic phosphorus

FPL_x = fraction of metabolized phosphorus by algal group x produced as labile particulate organic phosphorus

FPRP = fraction of predated phosphorus produced as refractory particulate organic phosphorus

FPLP = fraction of predated phosphorus produced as labile particulate organic phosphorus

APC = mean algal phosphorus-to-carbon ratio for all algal groups (g P per g C)

K_{RPOP} = hydrolysis rate of refractory particulate organic phosphorus (day⁻¹)

K_{LPOP} = hydrolysis rate of labile particulate organic phosphorus (day⁻¹)

WRPOP = external loads of refractory particulate organic phosphorus (g P day⁻¹)

WLPOP = external loads of labile particulate organic phosphorus (g P day⁻¹).

4.5.2 Dissolved Organic Phosphorus

Sources and sinks for dissolved organic phosphorus included in the model are (Fig. 4-1):

- algal basal metabolism and predation
- dissolution from refractory and labile particulate organic phosphorus
- mineralization to phosphate phosphorus

- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial DOP}{\partial t} = & \sum_{x=c,d,g,m} (FPD_x \cdot BM_x + FPDp \cdot PR_x) APC \cdot B_x \\ & + K_{RPOP} \cdot RPOP + K_{LPOP} \cdot LPOP - K_{DOP} \cdot DOP + \frac{WDOP}{V} \end{aligned} \quad (4-37)$$

DOP = concentration of dissolved organic phosphorus (g P m⁻³)

FPD_x = fraction of metabolized phosphorus by algal group x produced as dissolved organic phosphorus

FPDP = fraction of predated phosphorus produced as dissolved organic phosphorus

K_{DOP} = mineralization rate of dissolved organic phosphorus (day⁻¹)

WDOP = external loads of dissolved organic phosphorus (g P day⁻¹).

4.5.3 Total Phosphate

For total phosphate that includes both dissolved and sorbed phosphate (Section 4.5.4), sources and sinks included in the model are (Fig. 4-1):

- algal basal metabolism, predation, and uptake
- mineralization from dissolved organic phosphorus
- settling of sorbed phosphate
- sediment-water exchange of dissolved phosphate for the bottom layer only
- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial PO4t}{\partial t} = & \sum_{x=c,d,g,m} (FPI_x \cdot BM_x + FPIP \cdot PR_x - P_x) APC \cdot B_x + K_{DOP} \cdot DOP \\ & + \frac{\partial}{\partial z} (WS_{TSS} \cdot PO4p) + \frac{BFPO4d}{\Delta z} + \frac{WPO4t}{V} \end{aligned} \quad (4-38)$$

PO4t = total phosphate (g P m⁻³) = PO4d + PO4p (4-39)

PO4d = dissolved phosphate (g P m⁻³)

PO4p = particulate (sorbed) phosphate (g P m⁻³)

FPI_x = fraction of metabolized phosphorus by algal group x produced as inorganic phosphorus

FPIP = fraction of predated phosphorus produced as inorganic phosphorus

WS_{TSS} = settling velocity of suspended solid (m day⁻¹), provided by the hydrodynamic model

BFPO4d = sediment-water exchange flux of phosphate (g P m⁻² day⁻¹), applied to the bottom layer only

WPO4t = external loads of total phosphate (g P day⁻¹).

In Eq. 4-38, if total active metal is chosen as a measure of sorption site, the settling velocity of total suspended solid, WS_{TSS} , is replaced by that of particulate metal, WS_s (Sections 4.5.4 and 4.10). The remainder of this section explains each term in Equations 4-35 to 4-38, except BFPO4d (benthic flux of dissolved orthophosphate), which is described in Chapter 5.

4.5.4 Total Phosphate System

Suspended and bottom sediment particles (clay, silt, and metal hydroxides) adsorb and desorb phosphate in river and estuarine waters. This adsorption-desorption process has been suggested to buffer phosphate concentration in water column and to enhance the transport of phosphate away from its external sources (Carritt and Goodgal 1954; Froelich 1988; Lebo 1991). To ease the computational complication due to the adsorption-desorption of phosphate, dissolved and sorbed phosphate are treated and transported as a single state variable. Therefore, the model phosphate state variable, total phosphate, is defined as the sum of dissolved and sorbed phosphate (Eq. 4-39), and the concentrations for each fraction are determined by equilibrium partitioning of their sum.

In CE-QUAL-ICM, sorption of phosphate to particulate species of metals including iron and manganese was considered based on a phenomenon observed in the monitoring data from the mainstem of the Chesapeake Bay: phosphate was rapidly depleted from anoxic bottom waters during the autumn reaeration event (Cercio and Cole 1993). Their hypothesis was that reaeration of bottom waters caused dissolved iron and manganese to precipitate, and phosphate sorbed to newly formed metal particles and rapidly settled to the bottom. One state variable, total active metal, in CE-QUAL-ICM was defined as the sum of all metals that act as sorption sites, and the total active metal was partitioned into particulate and dissolved fractions via an equilibrium partitioning coefficient (Section 4.10). Then phosphate was assumed to sorb to only the particulate fraction of the total active metal.

In the treatment of phosphate sorption in CE-QUAL-ICM, the particulate fraction of metal hydroxides was emphasized as a sorption site in bottom waters under anoxic conditions. Phosphorus is a highly particle-reactive element, and phosphate in solution reacts quickly with a wide variety of surfaces, being taken up by and released from particles (Froelich 1988). The present model has two options, total suspended solid and total active metal, as a measure of a sorption site for phosphate, and dissolved and sorbed fractions are determined by equilibrium partitioning of their sum as a function of total suspended solid or total active metal concentration:

$$\begin{aligned}
 PO4p &= \frac{K_{PO4p} \cdot TSS}{1 + K_{PO4p} \cdot TSS} PO4t \quad \text{or} \quad PO4p = \frac{K_{PO4p} \cdot TAMp}{1 + K_{PO4p} \cdot TAMp} PO4t \\
 PO4d &= \frac{1}{1 + K_{PO4p} \cdot TSS} PO4t \quad \text{or} \quad PO4d = \frac{1}{1 + K_{PO4p} \cdot TAMp} PO4t
 \end{aligned} \tag{4-40}$$

$$= PO4t - PO4p \quad (4-41)$$

K_{PO4p} = empirical coefficient relating phosphate sorption to total suspended solid (per g m⁻³) or particulate total active metal (per mol m⁻³) concentration

TAMp = particulate total active metal (mol m⁻³).

Dividing Eq. 4-40 by Eq. 4-41 gives:

$$K_{PO4p} = \frac{PO4p}{PO4d} \frac{1}{TSS} \quad \text{or} \quad K_{PO4p} = \frac{PO4p}{PO4d} \frac{1}{TAMp} \quad (4-42)$$

where the meaning of K_{PO4p} becomes apparent, i.e., the ratio of sorbed to dissolved phosphate per unit concentration of total suspended solid or particulate total active metal (i.e., per unit sorption site available).

4.5.5 Algal Phosphorus-to-Carbon Ratio (APC)

Algal biomass is quantified in units of carbon per volume of water. In order to express the effects of algal biomass on phosphorus and nitrogen, the ratios of phosphorus-to-carbon and nitrogen-to-carbon in algal biomass must be specified. Although global mean values of these ratios are well known (Redfield et al. 1963), algal composition varies especially as a function of nutrient availability. As phosphorus and nitrogen become scarce, algae adjust their composition so that smaller quantities of these vital nutrients are required to produce carbonaceous biomass (DiToro 1980; Parsons et al. 1984). Examining the field data from the surface of upper Chesapeake Bay, Cerco and Cole (1993) showed that the variation of nitrogen-to-carbon stoichiometry was small and thus used a constant algal nitrogen-to-carbon ratio, ANC_x . Large variations, however, were observed for algal phosphorus-to-carbon ratio indicating the adaptation of algae to ambient phosphorus concentration (Cerco and Cole 1993): algal phosphorus content is high when ambient phosphorus is abundant and is low when ambient phosphorus is scarce. Thus, a variable algal phosphorus-to-carbon ratio, APC, is used in model formulation. A mean ratio for all algal groups, APC, is described by an empirical approximation to the trend observed in field data (Cerco & Cole 1994):

$$APC = (CP_{prm1} + CP_{prm2} \cdot \exp[-CP_{prm3} \cdot PO4d])^{-1} \quad (4-43)$$

CP_{prm1} = minimum carbon-to-phosphorus ratio (g C per g P)

CP_{prm2} = difference between minimum and maximum carbon-to-phosphorus ratio (g C per g P)

CP_{prm3} = effect of dissolved phosphate concentration on carbon-to-phosphorus ratio (per g P m⁻³).

4.5.6 Effect of Algae on Phosphorus

The terms within summation (Σ) in Equations 4-35 to 4-38 account for the effects of algae on phosphorus. Both basal metabolism (respiration and excretion) and predation are considered, and thus formulated, to contribute to organic and phosphate phosphorus. That is, the total loss by basal metabolism ($BM_x \cdot B_x$ in Eq. 4-5) is distributed using distribution coefficients; FPR_x , FPL_x , FPD_x , and FPI_x . The total loss by predation ($PR_x \cdot B_x$ in Eq. 4-5), is also distributed using distribution coefficients; $FPRP$, $FPLP$, $FPDP$, and $FPIP$. The sum of four distribution coefficients for basal metabolism should be unity, and so is that for predation. Algae take up dissolved phosphate for growth, and algae uptake of phosphate is represented by $(-\Sigma P_x \cdot APC \cdot B_x)$ in Eq. 4-38.

4.5.7 Mineralization and Hydrolysis

The third term on the RHS of Equations 4-35 and 4-36 represents hydrolysis of particulate organic phosphorus, and the last term in Eq. 3-7 represents mineralization of dissolved organic phosphorus. Mineralization of organic phosphorus is mediated by the release of nucleotidase and phosphatase enzymes by bacteria (Chróst and Overbek 1987) and algae (Boni et al. 1989). Since the algae themselves release the enzymes and bacterial abundance is related to algal biomass, the rate of organic phosphorus mineralization is related to algal biomass in model formulation. Another mechanism included in model formulation is that algae stimulate production of an enzyme that mineralizes organic phosphorus to phosphate when phosphate is scarce (Chróst and Overbek 1987; Boni et al. 1989). The formulations for hydrolysis and mineralization rates including these processes are:

$$K_{RPOP} = (K_{RP} + \frac{KHP}{KHP + PO4d} K_{RPalg} \Sigma_{x=c,d,g} B_x) \cdot \exp(KT_{HDR}[T - TR_{HDR}]) \quad (4-44)$$

$$K_{LPOP} = (K_{LP} + \frac{KHP}{KHP + PO4d} K_{LPalg} \Sigma_{x=c,d,g} B_x) \cdot \exp(KT_{HDR}[T - TR_{HDR}]) \quad (4-45)$$

$$K_{DOP} = (K_{DP} + \frac{KHP}{KHP + PO4d} K_{DPalg} \Sigma_{x=c,d,g} B_x) \cdot \exp(KT_{MNL}[T - TR_{MNL}]) \quad (4-46)$$

K_{RP} = minimum hydrolysis rate of refractory particulate organic phosphorus (day^{-1})

K_{LP} = minimum hydrolysis rate of labile particulate organic phosphorus (day^{-1})

K_{DP} = minimum mineralization rate of dissolved organic phosphorus (day^{-1})

K_{RPalg} , K_{LPalg} = constants that relate hydrolysis of refractory and labile particulate organic phosphorus, respectively, to algal biomass (day^{-1} per g C m^{-3})

K_{DPalg} = constant that relates mineralization to algal biomass (day^{-1} per g C m^{-3})

KHP = mean half-saturation constant for algal phosphorus uptake (g P m^{-3}).

$$= \frac{1}{3} \Sigma_{x=c,d,g} KHP_x \quad (4-47)$$

When phosphate is abundant relative to KHP, the rates become close to the minimum values with little influence from algal biomass. When phosphate becomes scarce relative to KHP, the rates increase with the magnitude of increase depending on algal biomass. Equations 4-44 to 4-46 have exponential functions that relate rates to temperature.

4.6 Nitrogen

The present model has five state variables for nitrogen: three organic forms (refractory particulate, labile particulate, and dissolved) and two inorganic forms (ammonium and nitrate). The nitrate state variable in the model represents the sum of nitrate and nitrite.

4.6.1 Particulate Organic Nitrogen

For refractory and labile particulate organic nitrogen, sources and sinks included in the model are (Figure 4-1):

- algal basal metabolism and predation
- dissolution to dissolved organic nitrogen
- settling
- external loads.

The kinetic equations for refractory and labile particulate organic nitrogen are:

$$\begin{aligned} \frac{\partial RPON}{\partial t} = & \sum_{x=c,d,g,m} (FNR_x \cdot BM_x + FNRP \cdot PR_x) ANC_x \cdot B_x - K_{RPON} \cdot RPON \\ & + \frac{\partial}{\partial z} (WS_{RP} \cdot RPON) + \frac{WRPON}{V} \end{aligned} \quad (4-48)$$

$$\begin{aligned} \frac{\partial LPON}{\partial t} = & \sum_{x=c,d,g,m} (FNL_x \cdot BM_x + FNLP \cdot PR_x) ANC_x \cdot B_x - K_{LPON} \cdot LPON \\ & + \frac{\partial}{\partial z} (WS_{LP} \cdot LPON) + \frac{WLPON}{V} \end{aligned} \quad (4-49)$$

RPON = concentration of refractory particulate organic nitrogen (g N m⁻³)

LPON = concentration of labile particulate organic nitrogen (g N m⁻³)

FNR_x = fraction metabolized nitrogen by algal group x as refractory particulate organic nitrogen

FNL_x = fraction of metabolized nitrogen by algal group x produced as labile particulate organic nitrogen

FNRP = fraction of predated nitrogen produced as refractory particulate organic nitrogen

FNLP = fraction of predated nitrogen produced as labile particulate organic nitrogen

ANC_x = nitrogen-to-carbon ratio in algal group x (g N per g C)

K_{RPON} = hydrolysis rate of refractory particulate organic nitrogen (day^{-1})

K_{LPON} = hydrolysis rate of labile particulate organic nitrogen (day^{-1})

WRPON = external loads of refractory particulate organic nitrogen (g N day^{-1})

WLPON = external loads of labile particulate organic nitrogen (g N day^{-1}).

4.6.2 Dissolved Organic Nitrogen

Sources and sinks for dissolved organic nitrogen included in the model are (Fig. 4-1):

- algal basal metabolism and predation
- dissolution from refractory and labile particulate organic nitrogen
- mineralization to ammonium
- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial DON}{\partial t} = & \sum_{x=c,d,g,m} (FND_x \cdot BM_x + FNDP \cdot PR_x) ANC_x \cdot B_x \\ & + K_{RPON} \cdot RPON + K_{LPON} \cdot LPON - K_{DON} \cdot DON + \frac{WDON}{V} \end{aligned} \quad (4-50)$$

DON = concentration of dissolved organic nitrogen (g N m^{-3})

FND_x = fraction of metabolized nitrogen by algal group x produced as dissolved organic nitrogen

FNDP = fraction of predated nitrogen produced as dissolved organic nitrogen

K_{DON} = mineralization rate of dissolved organic nitrogen (day^{-1})

WDON = external loads of dissolved organic nitrogen (g N day^{-1}).

4.6.3 Ammonium Nitrogen

Sources and sinks for ammonia nitrogen included in the model are (Fig. 4-1):

- algal basal metabolism, predation, and uptake
- mineralization from dissolved organic nitrogen
- nitrification to nitrate
- sediment-water exchange for the bottom layer only
- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial NH4}{\partial t} = & \sum_{x=c,d,g,m} (FNI_x \cdot BM_x + FNIP \cdot PR_x - PN_x \cdot P_x) ANC_x \cdot B_x + K_{DON} \cdot DON \\ & - Nit \cdot NH4 + \frac{BFNH4}{\Delta z} + \frac{WNH4}{V} \end{aligned} \quad (4-51)$$

FNI_x = fraction of metabolized nitrogen by algal group x produced as inorganic nitrogen

$FNIP$ = fraction of predated nitrogen produced as inorganic nitrogen

PN_x = preference for ammonium uptake by algal group x ($0 \leq PN_x \leq 1$)

Nit = nitrification rate (day^{-1}) given in Eq. 4-59

$BFNH4$ = sediment-water exchange flux of ammonium ($\text{g N m}^{-2} \text{ day}^{-1}$), applied to the bottom layer only

$WNH4$ = external loads of ammonium (g N day^{-1}).

4.6.4 Nitrate Nitrogen

Sources and sinks for nitrate nitrogen included in the model are (Fig. 4-1):

- algal uptake
- nitrification from ammonium
- denitrification to nitrogen gas
- sediment-water exchange for the bottom layer only
- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial NO3}{\partial t} = & - \sum_{x=c,d,g,m} (1 - PN_x) P_x \cdot ANC_x \cdot B_x + Nit \cdot NH4 - ANDC \cdot Denit \cdot DOC \\ & + \frac{BFNO3}{\Delta z} + \frac{WNO3}{V} \end{aligned} \quad (4-52)$$

$ANDC$ = mass of nitrate nitrogen reduced per mass of dissolved organic carbon oxidized ($0.933 \text{ g N per g C}$ from Eq. 4-33)

$BFNO3$ = sediment-water exchange flux of nitrate ($\text{g N m}^{-2} \text{ day}^{-1}$), applied to the bottom layer only

$WNO3$ = external loads of nitrate (g N day^{-1}).

The remainder of this section explains each term in Equations 4-48 to 4-52, except $BFNH4$ and $BFNO3$ which are described in Chapter 5.

4.6.5 Effect of Algae on Nitrogen

The terms within summation (\sum) in Equations 4-48 to 4-52 account for the effects of algae on nitrogen. As in phosphorus, both basal metabolism (respiration and excretion) and predation are considered, and thus formulated, to contribute to organic and ammonium nitrogen. That is, algal nitrogen released by both basal metabolism and predation are represented by distribution coefficients; FNR_x , FNL_x , FND_x , FNI_x , $FNRP$, $FNLP$, $FNDP$, and $FNIP$. The sum of four distribution coefficients for basal metabolism should be unity; the sum of the predation distribution coefficients should also be unity.

Algae take up ammonium and nitrate for growth, and ammonium is preferred from thermodynamic considerations. The preference of algae for ammonium is expressed as:

$$PN_x = NH4 \frac{NO3}{(KHN_x + NH4)(KHN_x + NO3)} + NH4 \frac{KHN_x}{(NH4 + NO3)(KHN_x + NO3)} \quad (4-53)$$

This equation forces the preference for ammonium to be unity when nitrate is absent, and to be zero when ammonium is absent.

4.6.6 Mineralization and Hydrolysis

The third term on the RHS of Equations 4-48 and 4-49 represents hydrolysis of particulate organic nitrogen and the last term in Eq. 4-50 represents mineralization of dissolved organic nitrogen. Including a mechanism for accelerated hydrolysis and mineralization during nutrient-limited conditions (Section 4.5.7), the formulations for these processes are:

$$K_{RPON} = (K_{RN} + \frac{KHN}{KHN + NH4 + NO3} K_{RNalg} \sum_{x=c,d,g} B_x) \cdot \exp(KT_{HDR}[T - TR_{HDR}]) \quad (4-54)$$

$$K_{LPON} = (K_{LN} + \frac{KHN}{KHN + NH4 + NO3} K_{LNalg} \sum_{x=c,d,g} B_x) \cdot \exp(KT_{HDR}[T - TR_{HDR}]) \quad (4-55)$$

$$K_{DON} = (K_{DN} + \frac{KHN}{KHN + NH4 + NO3} K_{DNalg} \sum_{x=c,d,g} B_x) \cdot \exp(KT_{MNL}[T - TR_{MNL}]) \quad (4-56)$$

K_{RN} = minimum hydrolysis rate of refractory particulate organic nitrogen (day^{-1})

K_{LN} = minimum hydrolysis rate of labile particulate organic nitrogen (day^{-1})

K_{DN} = minimum mineralization rate of dissolved organic nitrogen (day^{-1})

K_{RNalg} , K_{LNalg} = constants that relate hydrolysis of refractory and labile particulate organic nitrogen, respectively, to algal biomass (day^{-1} per g C m^{-3})

K_{DNalg} = constant that relates mineralization to algal biomass (day^{-1} per g C m^{-3})

KHN = mean half-saturation constant for algal nitrogen uptake (g N m^{-3}).

$$= \frac{1}{3} \sum_{x=c,d,g} KHN_x \quad (4-57)$$

Equations 4-54 to 4-56 have exponential functions that relate rates to temperature.

4.6.7 Nitrification

Nitrification is a process mediated by autotrophic nitrifying bacteria that obtain energy through the oxidation of ammonium to nitrite and of nitrite to nitrate. The stoichiometry of complete reaction is (Bowie et al. 1985):



The first term in the second line of Eq. 4-51 and its corresponding term in Eq. 4-52 represent the effect of nitrification on ammonium and nitrate, respectively. The kinetics of complete nitrification process are formulated as a function of available ammonium, dissolved oxygen and temperature:

$$Nit = \frac{DO}{KHNit_{DO} + DO} \frac{NH_4}{KHNit_N + NH_4} Nit_m f_{Nit}(T) \quad (4-59)$$

$$\begin{aligned} f_{Nit}(T) &= \exp(-KNit1[T - TNit]^2) & \text{if } T \leq TNit \\ &= \exp(-KNit2[TN - T]^2) & \text{if } T > TNit \end{aligned} \quad (4-60)$$

$KHNit_{DO}$ = nitrification half-saturation constant for dissolved oxygen (g O₂ m⁻³)

$KHNit_N$ = nitrification half-saturation constant for ammonium (g N m⁻³)

Nit_m = maximum nitrification rate at TN_{it} (g N m⁻³ day⁻¹)

TN_{it} = optimum temperature for nitrification (°C)

$KNit1$ = effect of temperature below TN_{it} on nitrification rate (°C⁻²)

$KNit2$ = effect of temperature above TN_{it} on nitrification rate (°C⁻²).

The Monod function of dissolved oxygen in Eq. 4-59 indicates the inhibition of nitrification at low oxygen level. The Monod function of ammonium indicates that when ammonium is abundant, the nitrification rate is limited by the availability of nitrifying bacteria. The effect of suboptimal temperature is represented using Gaussian form.

4.6.8 Denitrification

The effect of denitrification on dissolved organic carbon was described in Section 4.4.5. Denitrification removes nitrate from the system in stoichiometric proportion to carbon removal as determined by Eq. 4-33. The last term in the first line of Eq. 4-52 represents this removal of nitrate.

4.7 Silica

The present model has two state variables for silica: particulate biogenic silica and available silica.

4.7.1 Particulate Biogenic Silica

Sources and sinks for particulate biogenic silica included in the model are (Fig. 4-1):

- diatom basal metabolism and predation
- dissolution to available silica
- settling
- external loads

The kinetic equation describing these processes is:

$$\frac{\partial SU}{\partial t} = (FSP_d \cdot BM_d + FSPP \cdot PR_d) ASC_d \cdot B_d - K_{SUA} \cdot SU + \frac{\partial}{\partial z}(WS_d \cdot SU) + \frac{WSU}{V} \quad (4-61)$$

SU = concentration of particulate biogenic silica (g Si m⁻³)

FSP_d = fraction of metabolized silica by diatoms produced as particulate biogenic silica

FSPP = fraction of predated diatom silica produced as particulate biogenic silica

ASC_d = silica-to-carbon ratio of diatoms (g Si per g C)

K_{SUA} = dissolution rate of particulate biogenic silica (day⁻¹)

WSU = external loads of particulate biogenic silica (g Si day⁻¹).

4.7.2 Available Silica

Sources and sinks for available silica included in the model are (Fig. 4-1):

- diatom basal metabolism, predation, and uptake
- settling of sorbed (particulate) available silica
- dissolution from particulate biogenic silica
- sediment-water exchange of dissolved silica for the bottom layer only
- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned} \frac{\partial SA}{\partial t} = & (FSI_d \cdot BM_d + FSIP \cdot PR_d - P_d) ASC_d \cdot B_d + K_{SUA} \cdot SU + \frac{\partial}{\partial z}(WS_{TSS} \cdot SAp) \\ & + \frac{BFSAd}{\Delta z} + \frac{WSA}{V} \end{aligned} \quad (4-62)$$

SA = concentration of available silica (g Si m⁻³) = SAd + SAp (4-63)

SAd = dissolved available silica (g Si m⁻³)

SAp = particulate (sorbed) available silica (g Si m⁻³)

FSI_d = fraction of metabolized silica by diatoms produced as available silica

FSIP = fraction of predated diatom silica produced as available silica

BFSAd = sediment-water exchange flux of available silica (g Si m⁻² day⁻¹), applied to bottom layer only

WSA = external loads of available silica (g Si day⁻¹).

In Eq. 4-62, if total active metal is chosen as a measure of sorption site, the settling velocity of total suspended solid, WS_{TSS}, is replaced by that of particulate metal, WS_s (Sections 4.7.3 and 4.10).

4.7.3 Available Silica System

Analysis of Chesapeake Bay monitoring data indicates that silica shows similar behavior as phosphate in the adsorption-desorption process (Cерco and Cole 1993). As in phosphate, therefore, available silica is defined to include both dissolved and sorbed fractions (Eq. 4-63). Treatment of available silica is the same as total phosphate, and the same method to partition dissolved and sorbed phosphate is used to partition dissolved and sorbed available silica:

$$SAp = \frac{K_{SAp} \cdot TSS}{1 + K_{SAp} \cdot TSS} SA \quad \text{or} \quad SAp = \frac{K_{SAp} \cdot TAMp}{1 + K_{SAp} \cdot TAMp} SA \quad (4-64)$$

$$SAd = \frac{1}{1 + K_{SAp} \cdot TSS} SA \quad \text{or} \quad SAd = \frac{1}{1 + K_{SAp} \cdot TAMp} SA$$

$$= SA - SAp \quad (4-65)$$

K_{SAp} = empirical coefficient relating available silica sorption to total suspended solid (per g m⁻³) or particulate total active metal (per mol m⁻³) concentration.

As in K_{PO4p} in Section 4.5.4, K_{SAp} is the ratio of sorbed to dissolved available silica per unit sorption site available.

4.7.4 Effect of Diatoms on Silica

In Equations 4-62 and 4-63, those terms expressed as a function of diatom biomass (B_d) account for the effects of diatoms on silica. As in phosphorus and nitrogen, both basal metabolism (respiration and excretion) and predation are considered, and thus formulated, to contribute to particulate biogenic and available silica. That is, diatom silica released by both basal metabolism and predation are represented by distribution coefficients; FSP_d , FSI_d , $FSPP$, and $FSIP$. The sum of two distribution coefficients for basal metabolism should be unity and so is that for predation. Diatoms require silica as well as phosphorus and nitrogen, and diatom uptake of available silica is represented by $(-P_d \cdot ASC_d \cdot B_d)$ in Eq. 4-63.

4.7.5 Dissolution

The term $(-K_{SUA} \cdot SU)$ in Eq. 4-62 and its corresponding term in Eq. 4-63 represent dissolution of particulate biogenic silica to available silica. The dissolution rate is expressed as an exponential function of temperature:

$$K_{SUA} = K_{SU} \cdot \exp(KT_{SUA}[T - TR_{SUA}]) \quad (4-66)$$

K_{SU} = dissolution rate of particulate biogenic silica at TR_{SUA} (day⁻¹)

KT_{SUA} = effect of temperature on dissolution of particulate biogenic silica (°C⁻¹)

TR_{SUA} = reference temperature for dissolution of particulate biogenic silica (°C).

4.8 Chemical Oxygen Demand

In the present model, chemical oxygen demand is the concentration of reduced substances that are oxidizable through inorganic means. The source of chemical oxygen demand in saline water is sulfide released from sediments. A cycle occurs in which sulfate is reduced to sulfide in the sediments and reoxidized to sulfate in the water column. In fresh water, methane is released to the water column by the sediment process model. Both sulfide and methane are quantified in units of oxygen demand and are treated with the same kinetic formulation. The kinetic equation, including external loads, if any, is:

$$\frac{\partial COD}{\partial t} = - \frac{DO}{KH_{COD} + DO} K_{COD} \cdot COD + \frac{BFCOD}{\Delta z} + \frac{WCOD}{V} \quad (4-67)$$

COD = concentration of chemical oxygen demand ($\text{g O}_2\text{-equivalents m}^{-3}$)

KH_{COD} = half-saturation constant of dissolved oxygen required for oxidation of chemical oxygen demand ($\text{g O}_2 \text{ m}^{-3}$)

K_{COD} = oxidation rate of chemical oxygen demand (day^{-1})

$BFCOD$ = sediment flux of chemical oxygen demand ($\text{g O}_2\text{-equivalents m}^{-2} \text{ day}^{-1}$), applied to bottom layer only

$WCOD$ = external loads of chemical oxygen demand ($\text{g O}_2\text{-equivalents day}^{-1}$).

An exponential function is used to describe the temperature effect on the oxidation rate of chemical oxygen demand:

$$K_{COD} = K_{CD} \cdot \exp(KT_{COD}[T - TR_{COD}]) \quad (4-68)$$

K_{CD} = oxidation rate of chemical oxygen demand at TR_{COD} (day^{-1})

KT_{COD} = effect of temperature on oxidation of chemical oxygen demand ($^{\circ}\text{C}^{-1}$)

TR_{COD} = reference temperature for oxidation of chemical oxygen demand ($^{\circ}\text{C}$).

4.9 Dissolved Oxygen

Sources and sinks of dissolved oxygen in the water column included in the model are (Fig. 4-1):

- algal photosynthesis and respiration
- nitrification
- heterotrophic respiration of dissolved organic carbon
- oxidation of chemical oxygen demand
- surface reaeration for the surface layer only
- sediment oxygen demand for the bottom layer only
- external loads.

The kinetic equation describing these processes is:

$$\begin{aligned}
 \frac{\partial DO}{\partial t} = & \sum_{x=c,d,g,m} \left((1.3 - 0.3 \cdot PN_x) P_x - (1 - FCD_x) \frac{DO}{KHR_x + DO} BM_x \right) AOCR \cdot B_x \\
 & - AONT \cdot Nit \cdot NH4 - AOCR \cdot K_{HR} \cdot DOC - \frac{DO}{KH_{COD} + DO} K_{COD} \cdot COD \\
 & + K_r (DO_s - DO) + \frac{SOD}{\Delta z} + \frac{WDO}{V}
 \end{aligned} \tag{4-69}$$

AONT = mass of dissolved oxygen consumed per unit mass of ammonium nitrogen nitrified (4.33 g O₂ per g N; see Section 4.9.2)

AOCR = dissolved oxygen-to-carbon ratio in respiration (2.67 g O₂ per g C; see Section 4.9.1)

K_r = reaeration coefficient (day⁻¹); the reaeration term is applied to the surface layer only

DO_s = saturated concentration of dissolved oxygen (g O₂ m⁻³)

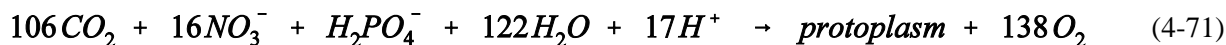
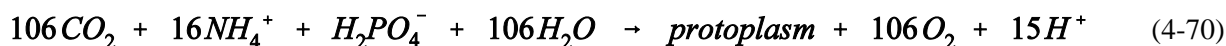
SOD = sediment oxygen demand (g O₂ m⁻² day⁻¹), applied to the bottom layer only; positive is to the water column

WDO = external loads of dissolved oxygen (g O₂ day⁻¹).

The two sink terms in Eq. 4-69, heterotrophic respiration and chemical oxygen demand, are explained in Section 4.4.4 (Eq. 4-29) and Section 4.8 (Eq. 4-67), respectively. The remainder of this section explains the effects of algae, nitrification, and surface reaeration.

4.9.1 Effect of Algae on Dissolved Oxygen

The first line on the RHS of Eq. 4-69 accounts for the effects of algae on dissolved oxygen. Algae produce oxygen through photosynthesis and consume oxygen through respiration. The quantity produced depends on the form of nitrogen utilized for growth. Equations describing production of dissolved oxygen are (Morel 1983):



When ammonium is the nitrogen source, one mole of oxygen is produced per mole of carbon dioxide fixed. When nitrate is the nitrogen source, 1.3 moles of oxygen are produced per mole of carbon dioxide fixed. The quantity, (1.3 - 0.3·PN_x), in the first term of Eq. 4-69 is the photosynthesis ratio and represents the molar quantity of oxygen produced per mole of carbon dioxide fixed. It approaches unity as the algal preference for ammonium approaches unity.

The last term in the first line of Eq. 4-69 accounts for the oxygen consumption due to algal respiration (Eq. 4-26). A simple representation of respiration process is:



from which, AOCR = 2.67 g O₂ per g C.

4.9.2 Effect of Nitrification on Dissolved Oxygen

The stoichiometry of nitrification reaction (Eq. 4-58) indicates that two moles of oxygen are required to nitrify one mole of ammonium into nitrate. However, cell synthesis by nitrifying bacteria is accomplished by the fixation of carbon dioxide so that less than two moles of oxygen are consumed per mole ammonium utilized (Wezernak and Gannon 1968), i.e., AONT = 4.33 g O₂ per g N.

4.9.3 Effect of Surface Reaeration on Dissolved Oxygen

The reaeration rate of dissolved oxygen at the air-water interface is proportional to the oxygen gradient across the interface, (DO_s - DO), when assuming the air is saturated with oxygen. The saturated concentration of dissolved oxygen, which decreases as temperature and salinity increase, is specified using an empirical formula (Genet et al. 1974):

$$DO_s = 14.5532 - 0.38217 \cdot T + 5.4258 \times 10^{-3} \cdot T^2 - CL \cdot (1.665 \times 10^{-4} - 5.866 \times 10^{-6} \cdot T + 9.796 \times 10^{-8} \cdot T^2) \quad (4-73)$$

CL = chloride concentration (mg/L) = S/1.80655.

The reaeration coefficient includes the effect of turbulence generated by bottom friction (O'Connor and Dobbins 1958) and that by surface wind stress (Banks and Herrera 1977):

$$K_r = \left(K_{ro} \sqrt{\frac{u_{eq}}{h_{eq}}} + W_{rea} \right) \frac{1}{\Delta z} \cdot KT_r^{T-20} \quad (4-74)$$

K_{ro} = proportionality constant = 3.933 in MKS unit

u_{eq} = weighted velocity over cross-section (m sec⁻¹) = $\sum(u_k V_k) / \sum(V_k)$

h_{eq} = weighted depth over cross-section (m) = $\sum(V_k) / B_\eta$

B_η = width at the free surface (m)

W_{rea} = wind-induced reaeration (m day⁻¹)

$$= 0.728 U_w^{1/2} - 0.317 U_w + 0.0372 U_w^2 \quad (4-75)$$

U_w = wind speed (m sec⁻¹) at the height of 10 m above surface

KT_r = constant for temperature adjustment of DO reaeration rate.

4.10 Total Active Metal

The present model requires simulation of total active metal for adsorption of phosphate and silica if that option is chosen (Fig. 4-1). The total active metal state variable is the sum of iron and manganese concentrations, both particulate and dissolved. In the model, the origin of total active metal is benthic sediments. Since sediment release of metal is not explicit in the sediment model (see Chapter 5), release is specified in the kinetic portion of the water column model. The only other term included is settling of the particulate fraction. Then the kinetic equation for total active metal, including external loads, if any, may be written as:

$$\frac{\partial TAM}{\partial t} = \frac{KHbmf}{KHbmf + DO} \frac{BFTAM}{\Delta z} e^{K_{tam}(T - T_{tam})} + \frac{\partial}{\partial z}(WS_s \cdot TAM_p) + \frac{WTAM}{V} \quad (4-76)$$

$$TAM = \text{total active metal concentration (mol m}^{-3}\text{)} = TAM_d + TAM_p \quad (4-77)$$

TAM_d = dissolved total active metal (mol m⁻³)

TAM_p = particulate total active metal (mol m⁻³)

$KHbmf$ = dissolved oxygen concentration at which total active metal release is half the anoxic release rate (g O₂ m⁻³)

$BFTAM$ = anoxic release rate of total active metal (mol m⁻² day⁻¹), applied to the bottom layer only

K_{tam} = effect of temperature on sediment release of total active metal (°C⁻¹)

T_{tam} = reference temperature for sediment release of total active metal (°C)

WS_s = settling velocity of particulate metal (m day⁻¹)

$WTAM$ = external loads of total active metal (mol day⁻¹).

In estuaries, iron and manganese exist in particular and dissolved forms depending on dissolved oxygen concentration. In the oxygenated water, most of the iron and manganese exist as particulate while under anoxic conditions, large fractions are dissolved, although solid-phase sulfides and carbonates exist and may predominate. The partitioning between particulate and dissolved phases is expressed using a concept that total active metal concentration must achieve a minimum level, which is a function of dissolved oxygen, before precipitation occurs:

$$TAM_d = \text{minimum}(TAM_{dmx} \cdot \exp(-K_{dotam} \cdot DO), TAM_t) \quad (4-78)$$

$$TAM_p = TAM - TAM_d \quad (4-79)$$

TAM_{dmx} = solubility of total active metal under anoxic conditions (mol m⁻³)

K_{dotam} = constant that relates total active metal solubility to dissolved oxygen (per g O₂ m⁻³).

4.11 Fecal Coliform Bacteria

Fecal coliform bacteria are indicative of organisms from the intestinal tract of humans and other animals and can be used as an indicator bacteria as a measure of public health (Thomann and Mueller 1987). In

the present model, fecal coliform bacteria have no interaction with other state variables, and have only one sink term, die-off. The kinetic equation, including external loads, may be written as:

$$\frac{\partial FCB}{\partial t} = - KFCB \cdot TFCB^{T-20} \cdot FCB + \frac{WFCB}{V} \quad (4-80)$$

FCB = bacteria concentration (MPN per 100 ml)

KFCB = first order die-off rate at 20°C (day⁻¹)

TFCB = effect of temperature on decay of bacteria (°C⁻¹)

WFCB = external loads of fecal coliform bacteria (MPN per 100 ml m³ day⁻¹).

4.12 Method of Solution

The kinetic equations for the 21 state variables in the EFDC water column water quality model can be expressed in a 21 × 21 matrix after linearizing some terms, mostly Monod type expressions:

$$\frac{\partial}{\partial t} [C] = [K] \cdot [C] + [R] \quad (4-81)$$

where [C] is in mass volume⁻¹, [K] is in time⁻¹, and [R] is in mass volume⁻¹ time⁻¹. Since the settling of particulate matter from the overlying cell acts as an input for a given cell, when Eq. 4-81 is applied to a cell of finite volume, it may be expressed as:

$$\frac{\partial}{\partial t} [C]_k = [K1]_k \cdot [C]_k + \lambda \cdot [K2]_k \cdot [C]_{k+1} + [R]_k \quad (4-82)$$

where the four matrices [C], [K1], [K2], and [R] are defined in Appendix A of Park et al. (1995). The subscript k designates a cell at the kth vertical layer. The layer index k increases upward with KC vertical layers; k = 1 is the bottom layer and k = KC is the surface layer. Then λ = 0 for k = KC; otherwise, λ = 1. The matrix [K2] is a diagonal matrix, and the non-zero elements account for the settling of particulate matter from the overlying cell.

Equation 4-82 is solved using a second-order accurate trapezoidal scheme over a time step of θ, which may be expressed as:

$$[C]_k^N = \left([I] - \frac{\theta}{2} [K1]_k^O \right)^{-1} \cdot \left([C]_k^O + \frac{\theta}{2} \{ [K1]_k^O \cdot [C]_k^O + \lambda [K2]_k^O \cdot [C]_{k+1}^A \} + \theta [R]_k^O \right) \quad (4-83)$$

where θ = 2 · m · Δt is the time step for the kinetic equations; [I] is a unit matrix; [C]^A = [C]^N + [C]^O; the superscripts O and N designate the variables before and after being adjusted for the relevant kinetic processes. Since Eq. 4-83 is solved from the surface layer downward, the term with [C]_{k+1}^A is known for the kth layer and thus placed on the RHS. In Eq. 4-83, inversion of a matrix can be avoided if the 21 state

variables are solved in a proper order. The kinetic equations are solved in the order of the variables in the matrix [C] defined in Appendix A of Park et al. (1995).

4.13 Macroalgae (Periphyton) State Variable

The EFDC water quality model was augmented to represent benthic attached algae (often referred to as macroalgae in estuarine waters and periphyton in fresh waters) using the existing framework for phytoplankton growth kinetics. Mathematical relationships based on the impacts of temperature, available light, available nutrients, stream velocity, and density-dependent interactions were incorporated into the algae growth kinetics framework within EFDC. The major differences between modeling techniques for attached and free-floating algae are: (1) attached algae are expressed in terms of areal densities rather than volumetric concentrations; (2) attached algae growth can be limited by the availability of bottom substrate; (3) the availability of nutrients to the macroalgae matrix can be influenced by stream velocity; and (4) macroalgae are not subject to hydrodynamic transport. A good description of periphyton kinetics as it relates to water quality modeling can be found in Warwick et al. (1997) and has been used to develop this section of the report.

A mass-balance approach was used to model macroalgae growth, with carbon serving as the measure of standing crop size or biomass. For each model grid cell the equation for macroalgae growth is slightly different than the one for free-floating algae (Eq. 4-6):

$$P_m = PM_m \cdot f_1(N) \cdot f_2(I) \cdot f_3(T) \cdot f_4(V) \cdot f_5(D) \quad (4-84)$$

where

- PM_m = maximum growth rate under optimal conditions for macroalgae
- $f_1(N)$ = effect of suboptimal nutrient concentration ($0 \leq f_1 \leq 1$)
- $f_2(I)$ = effect of suboptimal light intensity ($0 \leq f_2 \leq 1$)
- $f_3(T)$ = effect of suboptimal temperature ($0 \leq f_3 \leq 1$)
- $f_4(V)$ = velocity limitation factor ($0 \leq f_4 \leq 1$)
- $f_5(D)$ = density-dependent growth rate reduction factor ($0 \leq f_5 \leq 1$).

The basic growth kinetics for macroalgae were developed from those supplied by EFDC and others developed by Runke (1985). The macroalgae population as a whole is characterized by the total biomass present without considering the different species and their associated environmental processes. The optimum growth for the given temperature is adjusted for light, nutrients, velocity, and density-dependent limitations. Each growth limitation factor can vary from 0 to 1. A value of 1 indicates the factor does not limit growth, and a value of 0 means the factor is so severely limiting that growth is stopped entirely (Bowie et al. 1985).

Stream velocity has a twofold effect on periphyton productivity in freshwater streams: velocity increases to a certain level to enhance biomass accrual, but further increases result in substantial scouring (Horner et al. 1990). A benthic algal population is typified as a plant community with an understory and an overstory. The entire community is called a matrix. As the matrix develops, the periphyton community is composed of an outer layer of photosynthetically active cells and inner layers of senescent and decomposing cells. Layering can also develop among different species of periphyton. Environmental conditions within the matrix are altered by the physical structure of the periphyton. This influences nutrient uptake and primary production rates of the algae (Sand-Jensen 1983). Above a certain level, current has a simulating effect on periphyton metabolism by mixing the overlying waters with nutrient-poor waters that develop around cells (Whitford and Schumacher 1964). The physical structure of the periphyton community and nutrient uptake by periphyton interfere with nutrient flux through the microbial matrix (Stevenson and Glover 1993).

Current is constantly scouring periphyton from its substrate. At high enough velocities, shear stress can result in substantial biomass reduction. Even at low velocities, sudden increases in velocity raise instantaneous loss rates substantially, but these high rates persist only briefly (Horner et al. 1990). An increase in velocity above that to which benthic algae are accustomed leads to increased loss rates and temporarily reduced biomass. However, recolonization and growth after biomass reduction are usually rapid. The effects of suboptimal velocity upon growth rate are represented in the model by a velocity limitation function. Two options are available in the model for specifying the velocity limitation: (1) a Michaelis-Menton (or Monod) equation (4-85) and (2) a five-parameter logistic function (4-86). The Monod equation limits macroalgae growth due to low velocities, whereas the five-parameter logistic function can be configured to limit growth due to either low or high velocities (Figure 4-2).

Velocity limitation option 1, the Michaelis-Menton equation, is written as follows:

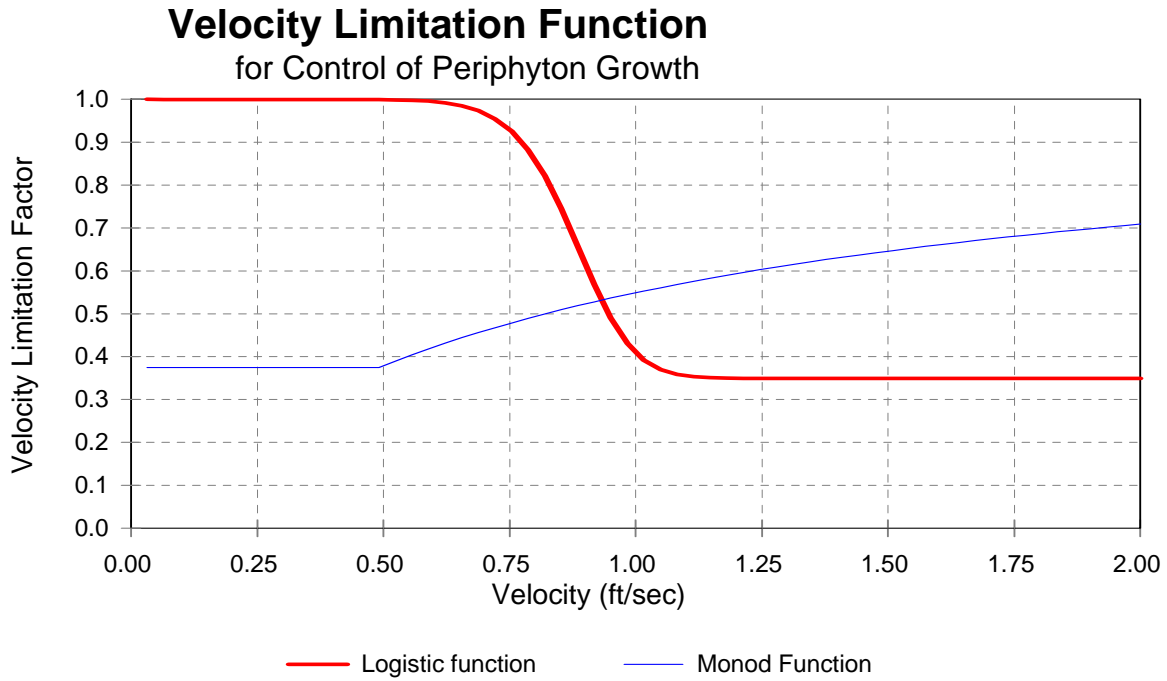


Figure 4-2. Velocity limitation function for (Option 1) the Monod equation where $KMV = 0.25$ m/sec and $KMV_{min}=0.15$ m/sec, and (Option 2) the five-parameter logistic function where $a=1.0$, $b=12.0$, $c=0.3$, $d=0.35$, and $e=3.0$ (high velocities are limiting)

$$f_4(V) = \frac{U}{KMV + U} \quad (4-85)$$

where

U = stream velocity (m/sec)
 KMV = half-saturation velocity (m/sec)

Velocity limitation option 2, the five-parameter logistic function is as follows:

$$f_4(V) = d + \frac{a - d}{\left[1 + \left(\frac{U}{c} \right)^b \right]^e} \quad (4-86)$$

where

U = stream velocity (m/sec)
 a = asymptote at minimum x
 b = slope after asymptote a
 c = x-translation

d = asymptote at maximum x

e = slope before asymptote d

The half-saturation velocity in Eq. 4-85 is the velocity at which half the maximum growth rate occurs. This effect is analogous to the nutrient limitation because the effect of velocity at suboptimal levels on periphyton growth is due to increasing the exchange of nutrients between the algal matrix and the overlying water (Runke 1985). However, this formula can be too limiting at low velocities. This function does not allow periphyton growth in still waters, but periphyton does grow in still waters such as lakes. Therefore, the function is applied only at velocities above a minimum threshold level (KMVmin). When velocities are at or below this lower level, the limitation function is applied at the minimum level. Above this velocity, the current produces a steeper diffusion gradient around the periphyton (Whitford and Schumacher 1964). A minimum formulation is used to combine the limiting factors for nitrogen, phosphorus, and velocity. The most severely limiting factor alone limits periphyton growth. Note that Eq. 4-86 can be configured so that low velocities are limiting by setting parameter d greater than parameter a , and vice versa to limit growth due to high velocities. In waters that are rich in nutrients, low velocities will not limit growth. However, high velocities may cause scouring and detachment of the macroalgae, resulting in a reduction in biomass. The five-parameter logistic function can be configured to approximate this reduction by limiting growth at high velocities.

Macroalgae (periphyton) growth can also be limited by the availability of suitable substrate (Ross 1983). Macroalgae communities reach maximum rates of primary productivity at low levels of biomass (McIntire 1973; Pfeifer and McDiffett 1975). The relationship between standing crop and production employs the Michaelis-Menton kinetic equation:

$$f_5(D) = \frac{KBP}{KBP + P_m} \quad (4-87)$$

where

KBP = half-saturation biomass level (g C/m²)

P_m = macroalgae biomass level (g C/m²).

The half-saturation biomass level (KBP) is the biomass at which half the maximum growth rate occurs. Caupp et al. (1991) used a KBP value of 5.0 g C/m² (assuming 50% of ash free dry mass is carbon) for a region of the Truckee River system in California. The function in Eq. 4-87 allows maximum rates of primary productivity at low levels of biomass with decreasing rates of primary productivity as the community matrix expands.